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Theoretical study of the electronic structure with dipole moment calculations of barium monofluoride

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ABSTRACT

The potential energy curves have been investigated for the 41 lowest doublet and quartet electronic states in the ${}^{2s+1}\Lambda^{\pm}$ representation below 55,000 cm^{-1} of the molecule BaF via CASSCF and MRCI (single and double excitations with Davidson correction) calculations. Twenty-five electronic states have been studied here theoretically for the first time. The crossing and avoided crossing of 20 doublet electronic states have been studied in the region 30,000–50,000 cm^{-1}. The harmonic frequency ω_e, the internuclear distance R_e, the rotational constant B_e, the electronic energy with respect to the ground state T_e, and the permanent and transition dipole moments have been calculated in addition to static dipole polarizability of the ground state. By using the canonical functions approach, the eigenvalue E_v, the rotational constant B_v, and the abscissas of the turning points R_{min} and R_{max} have been calculated for the electronic states up to the vibrational level $v=98$. The comparison of these values with the theoretical results available in the literature shows a very good agreement.

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1. Introduction

The alkaline earth monofluoride molecules have a common $X^2\Sigma^+$ ground state, one unpaired electron, and they are considered to be very ionic. An ionic model can provide a simple and powerful tool for the understanding of ionic compounds in terms of the properties of their constituent atomic ions. These models have been extended and modified to describe small molecules and molecular aggregates, including diatomics, triatomics, clusters and molecular ions. Among the diatomics, the group of alkaline earth monohalides is of particular interest. The electronic structure of these species may be described as a single valence electron outside two closed shell ions: a halogenoide anion X^- and an alkaline earth cation Y^+. The electron is localized around the metal ion and polarized by the field of X^-. Analysis of the electronic structure of the alkaline earth monohalides has received a great deal of attention [1–21]. The barium monofluoride (BaF) molecule is one of these species which is studied experimentally in the literature [11,14] and theoretically [22–24]. In the literature, 16 electronic states have been obtained experimentally for the doublet multiplicity states $X^2\Sigma^+$, $(A')^2\Delta$, $(A)^2\Pi$, $(B)^2\Sigma^+$, $(C)^2\Pi$, $(D)^2\Sigma^+$, $(D')^2\Sigma^+$, $(E')^2\Pi$, $(E'')^2\Pi$, $(E)^2\Sigma^+$, $(F)^2\Pi$, $(G)^2\Sigma^+$, $(H)^2\Sigma^+$, $(I)^2\Sigma^+$, $(J)^2\Pi$, and $(K)^2\Pi$ and no results have been reported for the quartet electronic states of the molecule BaF. According to the experimental work of Jakubek et al. [25], $(G)^2\Sigma^+$ and $(H)^2\Sigma^+$ states have been located in the region: 31,460–32,400 cm^{-1} and they believe that the state $(I)^2\Sigma^+$ belongs to a species other than the BaF molecule.

The electronic states arise from excitation of a single nonbonding electron to higher-lying orbitals. Some of these electronic states can be arranged into Rydberg series and it is particularly interesting to determine which Rydberg orbitals are responsible for the observed electronic states.

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However, data are lacking for the molecular electronic states and potential energy curves of the BaF molecule. The present paper deals with the potential energy curves of various observed electronic states and the estimation of the ground-state dissociation energy of this molecule. Providing an accurate calculation of the properties for the $X^2\Sigma^+$ ground state reveals the strength of the dipolar interactions for the BaF system. Investigations of the potential energy curves with vibration-rotation study for the low-lying excited states allow us to predict strong transitions from highly electronic states to the absolute vibronic ground state. These transitions allow the production of stable ultracold polar molecules. In addition, investigation of adiabatic passages for experiments requires presenting high-lying adiabatic energy curves, which is also important for the enhancement of nonlinear processes and for many laser cooling applications. So we investigate in this work the 41 lowest doublet and quartet electronic states in the $^{2s+1}\Lambda^{\pm}$ representation below 55,000 cm^{-1} of the molecule BaF. This calculation has been performed via Complete Active Space Self-Consistent Field (CASSCF) and MRCI (single and double excitation with Davidson correction) calculations where we found that the ground state is $X^2\Sigma^+$. Avoided crossings have been noticed in the regions: 40,000 cm^{-1} and 49,000 cm^{-1} for the states $^2\Sigma^+$ and $^2\Delta$, 30,000 cm^{-1} and 50,000 cm^{-1} between $^2\Pi$ states, 53,000 cm^{-1} and 55,000 cm^{-1} between the states $(5)^4\Pi$ and $(6)^4\Pi$.

The potential energy curves (PECs), along with the transition energy with respect to the minimum energy for the ground state T_e, the equilibrium internuclear distance R_e, the harmonic frequency ω_e, the rotational constant B_e, and the static dipole moment μ have been obtained for the low-lying doublet and quartet electronic states of the BaF molecule. The transition dipole moments have been also computed between the ground electronic state and the excited electronic states. In addition, the static dipole polarizability α_D has also been calculated for the ground state $X^2\Sigma^+$. Taking advantage of the electronic structure of the investigated electronic states and by using the canonical functions approach, the eigenvalue E_v, the rotational constant B_v, and the abscissas of the turning points R_{min} and R_{max} have been calculated for several vibrational levels of the considered electronic states. Twenty-five states have been investigated here for the first time.

2. Computational approach

Representations of the effective potential energy of a diatomic molecule as a function of the internuclear distance, usually referred to as potential energy curves, are characteristics of molecular states. These curves form a convenient way of displaying the energy levels of diatomic molecules and are of considerable importance in understanding the kinetic mechanics, spectral phenomena, stellar structure and other associated problems. These curves are calculated using *ab initio* techniques.

To test the use of the *ab initio* calculation for the study of the alkaline earth monohalides, particularly barium atom mono-fluorine, we investigate in the present work the lowest-lying doublet and quartet electronic states of the BaF molecule via the CASSCF method. Multireference CI calculations (single and double excitations with Davidson corrections) were performed. The barium atom is treated as a system with 10 electrons by using the effective core potential CRENBL ECP basis given by Ross et al. [26] for *s*, *p*, and *d* functions to obtain the basis set (5*s*,5*p*,4*d*) for the Ba atom. The fluorine species is treated in all electron schemes where the 9 electrons are considered using a VDZ Valence Double Zeta 3-21G basis given by Binkley et al. [27] for *s* and *p* functions to obtain the basis set (6*s*,3*p*)→[3*s*,2*p*] for the F atom. We will designate throughout this paper these two basis sets as Basis 1. All the basis sets used in the present work have been obtained from the Basis Set Exchange (BSE) website and EMSL basis set library [28–29]. The *ab initio* calculation with the 19 electrons left outside the effective core potential of this molecule has been done in the following way: 14 inner electrons were frozen in subsequent calculations so that five valence electrons were explicitly treated. The active space contains 5σ (Ba: $5d_0$, $6p_0$; F: $2p_0$, 3*s*, $3p_0$), 4π (Ba: $5d_{\pm1}$, $6p_{\pm1}$; F: $2p_{\pm1}$, $3p_{\pm1}$), and 1δ (Ba: $5d_{\pm2}$) orbitals in the C_{2v} symmetry distributed into irreducible representation a_1, b_1, b_2, and a_2 in the following way $6a_1$, $4b_1$, $4b_2$, and $1a_2$ noted by [6,4,4,1]. In the range of the internuclear distance R around the equilibrium position of its ground state, the BaF molecule is assumed to be mainly ionic. This calculation has been performed via the computational chemistry program MOLPRO [30] taking advantage of the graphical user interface GABEDIT [31].

3. Results and discussions

3.1. ab initio Calculations

In the present work, the potential energy curves (PECs) and the permanent dipole moments (PDMs) for 41 doublet and quartet states in the representation $^{2s+1}\Lambda^{\pm}$ have been calculated for 326 internuclear distances in the range $1.50\ \text{Å} \le R \le 8.00\ \text{Å}$ of Basis 1. These PECs and PDMs of the different symmetries are given in Figs. 1–4 and Figs. 6–9, respectively. In the range of *R* considered, some crossings and avoided crossings between different electronic states occur; the positions of these crossings are given in Table 1 and those of avoided crossing are given in Table 2.

In Figs. 1, 2, and 4, the PECs show avoided crossings in the interval 2.08 Å and 4.42 Å for the doublet states and at $R=2.28$ Å and $R=3.54$ Å for the $^4\Pi$ states (Table 2). If the two potential energy curves correspond to electronic states of different symmetry, the crossing is strictly allowed and their wavefunctions are adiabatic solutions of the Schrödinger equation. But if these wavefunctions have the same symmetry, they will mix with each other to give two adiabatic solutions which no longer cross and the crossing becomes avoided. These adiabatic solutions of the Schrödinger equation are obtained by linear combinations of the diabatic ones where the variation method is used. Such crossings or avoided crossings can dramatically alter the stability of the molecule.

In Table 3, the spectroscopic constants such as the vibrational harmonic constant ω_e, the internuclear distance at equilibrium R_e, the rotational constant B_e, and the

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